Effects of Annealing Electrodeposited Bismuth Telluride Films

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Abstract

Thermoelectric thin films exhibit different qualities when compared with bulk materials. The goal however is to achieve thermoelectric properties of bulk materials from electrodeposited thin films. Thin films are produced by electrochemical deposition at room temperature. In order to optimize thermoelectric figure of merit proper carrier concentration must be obtained. The carrier concentration can be observed through resistivity measurements of thin film Bi_2Te_3 n-type depositions on thin Chromium-Gold substrates. Seebeck coefficient measurements are performed on Bi_2Te_3 n-type thin films deposited on Molybdenum foil. Annealing samples in the presence of Hydrogen Argon forming gas increases thermopower and resistivity consistent with a decrease in carrier concentration. Annealing between 200 and 500 Celsius for 1 to 20 hours was tested. This produces films with resistivity of 1 mΩ cm but a Seebeck coefficient of only –60 μV/K. Samples are suspected of remaining too heavily doped even after annealing. These results suggest there are defects in thin films that cannot be removed by annealing alone.

Introduction

Carrier concentration is important in optimizing thermoelectric figure of merit. If carrier concentration is too low, resistivity of the semiconductor is too high. When carrier concentration is too high the Seebeck coefficient decreases. Resistivity, ρ, varies according to

$$\rho = 1 / (n e mu) \quad (1)$$

In equation (1) ***n*** is carrier concentration, ***e*** is electron charge, and ***mu*** is mobility. Seebeck coefficient varies according to Log (1 / ***n***) making the optimal carrier concentration approximately 10^19/cc. Optimal resistivity and Seebeck values are approximately 1 mOhm cm and -200 μV/K respectively.

Thin films (5-60 μm thick) are electrochemically deposited onto a substrate using a three electrode open cell configuration with factors like thickness, composition, and doping being easily controlled. The goal is to achieve bulk ***ZT*** in thin films because electrochemical deposition is the preferred method of fabrication [1-3].

Two factors, the film substrate and the thickness of the film largely affect measurements on thin films. Resistivity measurements are optimum on insulating substrates as no corrections need be made for the effect of the substrate. Electrodeposited thin films however must be deposited on conducting substrates such as thin gold metallized substrates. In this case the film and substrate behave as a parallel combination of resistors. Thus if the substrate resistance, R_{Sub}, is known then the resistance of the film, R_f, can be calculated

$$R_f = R_m R_{Sub} / (R_{Sub} - R_m) \quad (2)$$

R_m is the measured resistance of the sample in Equation (2). Resistivity in thin films is also a function of film thickness. As film thickness decreases, there is a sharp rise in resistivity due to decreases in grain size and lower crystallinity. [4]

When measuring Seebeck coefficient, the contribution of the substrate to the measurement decreases as substrate Seebeck coefficient decreases. The Seebeck coefficient is also shown to vary inversely with film thickness. [4]

Annealing samples to remove defects in crystal structure is common. Annealed samples exhibit an increase in Seebeck coefficient. This increase in Seebeck coefficient produces increased resistivity as well. Thermoelectric figure of merit however will increase due to the greater contribution from the Seebeck coefficient.

ECD, Resistivity and Seebeck Measurements

Electrochemical depositions (ECD) are done in an open cell three electrode configuration. Depositions are performed at room temperature on either Molybdenum or Chromium-Gold on glass substrates.

Samples are attached to an aluminum alligator clip with a copper wire soldered to one end. The clip is then coated in parafilm and nail polish in order to ensure that only the substrate is exposed to the solution. The substrate acts as the working electrode during the deposition. The counter electrode consists of a Platinum mesh screen. A Standard Calomel Electrode (SCE) serves as the reference electrode.

The deposition is performed in an acidic Bismuth-Telluride solution. All depositions are done in 8 mM Bismuth, 10 mM Telluride dissolved in acidic solution (pH 0) of HNO_3 and deionized water. The SCE is placed in 1 M KNO_3 and is electrically connected to the Bismuth-Telluride solution using a KNO_3 saturated salt bridge.

An EGG Potentiostat / Galvanostat 273A controls the deposition process. All depositions are performed at constant potential of –8 mV. Deposition times varied depending on the desired film thickness. Completed samples are rinsed in Acetone and deionized water.

In order to negate the effect of the substrate on resistivity measurements numerous attempts were made to delaminate Bi_2Te_3 films onto insulating substrates. Attempts were made to delaminate films onto Alumina using hot wax and onto stainless steel using clear tape.

Chromium-Gold and Titanium-Gold sputtered on glass substrates are used for resistance measurements. Resistance measurements are performed in vacuum using a four point Van der Pauw method. Contacts are made using either Indium or silver paint. Data is taken as a function of temperature until there is an obvious problem with the electrical contacts. Using this data along with the measured resistance for Chromium-Gold metallizations, a parallel resistance is calculated for each film. The thickness of each film is measured using an alpha step method. Resistivity is calculated using the metallization resistance and measured thickness of each sample. Some samples are annealed in vacuum while others are annealed in the presence of 2/3-atmosphere Hydrogen Argon forming gas.

Molybdenum depositions are used for Seebeck coefficient measurements. Seebeck measurements, both before and after annealing processes, are performed slightly below room temperature using a hot and cold side thermocouple and voltmeter. Samples are annealed in 2/3- atmosphere Hydrogen Argon forming gas and are heated to 105° Celsius for one hour prior to annealing at specified temperature and time.

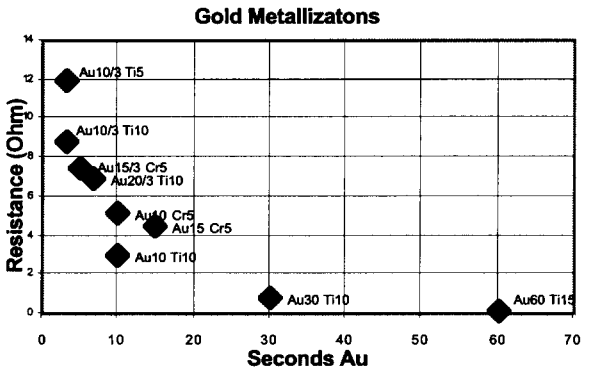

Figure 1. Parallel resistance values for various gold metallizations.

Results and Discussion

Resistivity measurements were performed on glass slides with sputtered Chromium-Gold or Titanium-Gold metallizations. In order to reduce the effect of the substrate in resistivity measurements, thin metallization are desired. Too thin a metallization, however, resulted in deficient deposition growth. The metallization resistances are plotted as a function of seconds of metallization in Figure 1. Au10 Cr5, highlighted in red, has a room temperature resistance of 5.11 Ohms provided a compromise between high resistance metallization compared to the film resistance and good film growth. The resistivity data presented was taken on Bi_2Te_3 films deposited on Au10 Cr5 metallizations.

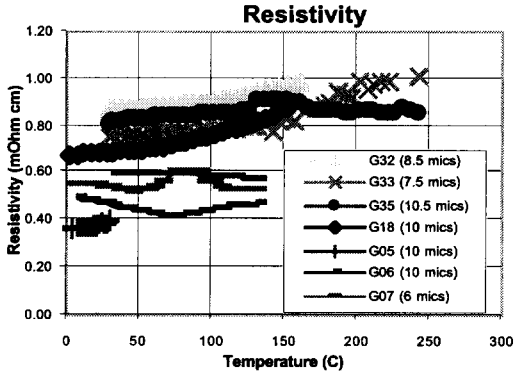

Figure 2. Resistivity values for thin Bismuth-Telluride film (as deposited).

Figure 2 shows resistivity data for samples (as deposited) from 30 to 230 degrees Celsius. As deposited, Bi_2Te_3 films generally had measured room temperature resistivities between 0.4 and 0.85 mOhm cm.

Resistivity increases when annealed (Figure 3). Samples are annealed at 240° C in either a vacuum or Hydrogen Argon environment. Annealed samples exhibit an increase in resistivity that slows after approximately 4 hours. After annealing, samples exhibit desired resistivity values of approximately 1 mOhm cm.

Problems with resistivity measurements arose with surface contact resistances. Indium contacts were insufficient for high temperature measurements (above 205° C) due to melting and oxidation. Silver paint contacts are an improvement however it is very difficult to make the point contacts that give the most accurate Van der Pauw measurements.

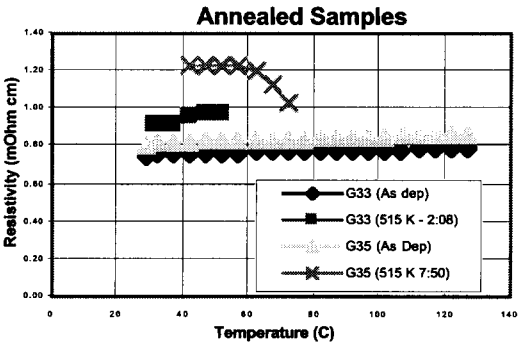

Figure 3. Resistivity values before and after annealing.

Both delamination techniques used proved impractical. Hot wax delamination produced either partial or cracked samples insufficient for measurement. Stainless steel delamination provided much cleaner samples however SEM analysis showed micron size cracking throughout the entire sample. This cracking resulted in inaccurate resistivity measurements higher than actual values. For this reason all resistivity data was taken from Chromium-Gold substrates.

Samples exhibited Seebeck coefficients between -35 and -45 μV/K as deposited. Annealing processes produced marginal improvements to approximately -60 μV/K and as high as –80 μV/K. All samples annealed at or above 235 Celsius for more than two hours exhibited similar marginal increases in Seebeck coefficient. Figure 4 shows three-hour annealing effects over temperatures ranging from 150 to 500 Celsius. Figure 5 displays annealing effects at 235 Celsius for time periods from 2 to 16 hours.

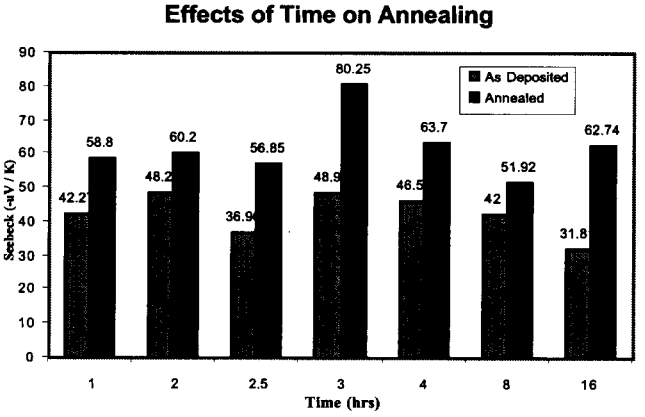

Figure 4. Seebeck values for samples with various annealing times.

The modest increase in Seebeck indicates some removal of defect dopants by annealing consistent with the increase in resistivity. However, these results are much lower than hoped, where the optimum Seebeck is about –200 μV/K.

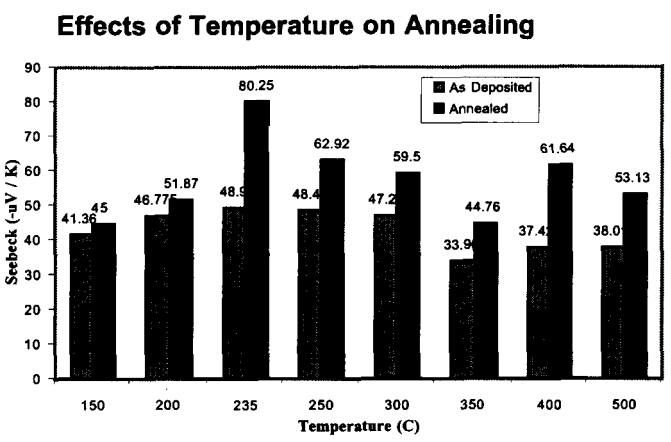

Figure 5. Seebeck values for samples with various annealing temperatures.

The low thermopower suggest that the films remain to heavily doped (too high carrier concentration) even after annealing. The annealing process may not only remove defects, but actually increase the doping by altering the stoichiometry. If bismuth or tellurium sublime out of the sample during annealing, dopant concentration may increase and the sample becomes too heavily doped, resulting in low Seebeck values. The visible deposits on the low temperature end of the annealing tube support this hypothesis.

Conclusions

Annealing of electrodeposited Bi_2Te_3 films produces a small but noticeable decrease in carrier concentration as evidenced by the increased resistivity and higher Seebeck coefficients. The increases in Seebeck are largely independent of annealing time and temperature.

Results indicate sublimation of the films may pose a problem with the annealing process used in these experiments. The process should be modified in order to prevent Bismuth or tellurium loss in samples during annealing, by placing Bi, Te or Bi_2Te_3 in the annealing tube. For the same reasons, it would be best to avoid large temperature gradients when annealing. It is also possible however that there are inherent defects in the films that cannot be removed by annealing alone, making it difficult to achieve bulk *ZT* values from electrochemically deposited thin films.

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